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SYNTHESIS AND PROPERTIES OF POLYPHTHALIMIDES

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16. Abstract Attempts were made to synthesize polymers containing benzophenone and phthalimides as main chain repeating units. In a polar solvent, a reaction was performed of aromatic diamines with dianhydrides (III) of tetracarboxylic acid (II) obtained by oxidizing products of the Friedle-Crafts' reaction between ortho-xylene and bis(chloromethyl) benzene (I), and soluble phthalimidic acid polymers were obtained. These were converted into polyphthalimides (IV) by heating for 4 hours at 220°C, producing yellow, flexible films. (IV) was subjected to ring opening in an alkali aqueous solution, producing polyamidic acid salts. It was confirmed from the IR spectra that these turned into polyamidic acids when given acid treatment. The electrical properties of the polymers were measured, and the dielectric constant displayed a large value of 6.1-7.8. In measurements with a thermobalance, the pyrolysis in the air began at a temperature close to 350°C and was more or less completed at 500°C.

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SYNTHESIS AND PROPERTIES OF POLYPHTHALIMIDES

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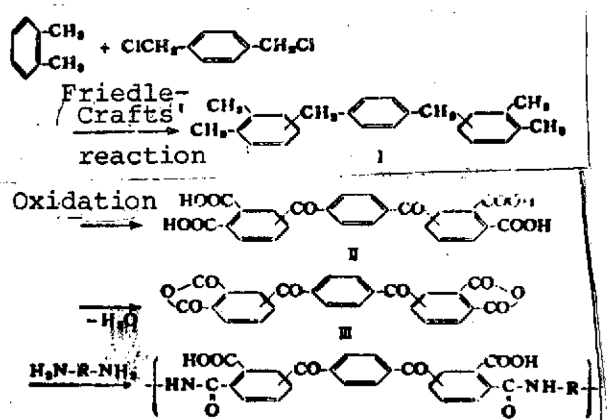
1. Introduction /1069*

It is well-known that the polypyromellitic imides obtained by ring closure condensation of products obtained by adding aromatic diamines to pyromellitic dianhydrides have a great thermal stability [1-4]. We attempted to synthesize polymers having a phthalimide ring instead of a pyromellitic imide ring in their main chain. Having obtained several findings concerning their thermal stability and other properties, we take this opportunity to report them.

The polyphthalimides were obtained by reaction between bis(phthalic anhydride) derivatives (III) and aromatic diamines in a polar solvent of N-methyl pyrrolidone. (III) was obtained by first causing a reaction between ortho-xylene and p-bis(chloromethyl)-benzene in the presence of a Friedle-Crafts' catalyst. This produced a bis(ortho-xylyl) derivative (I), which was then oxidized. We used p,p-diaminodiphenyl ether or p,p-diphenylmethane as the aromatic diamine.



(1)

[equation 1 continued]

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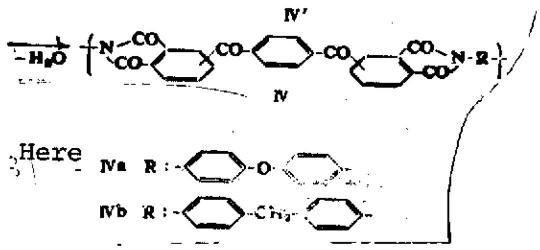

(1)

2. Experiments

2.1. Synthesis of bis(phthalic anhydride) Derivative (III)

Synthesis of bis(ortho-xylyl) Derivative (I)

Thirty-five grams (0.2 mol) of p-bis(chloromethyl) benzene and 424 g (4 mol) of ortho-xylene were taken into a flask with four mouths, and 0.4 g of acetylacetone ferrous complex salt was added. The mixture was stirred for 3 hours during heating and reflux. After cooling, it was washed three times with concentrated hydrochloric acid. Next, rinsing was repeated. After drying with calcium chloride, the unreacted ortho-xylene was removed by distillation, and fractional distillation was performed at reduced pressure. The fraction at bp 240-250°C/0.1-0.2 mm Hg was solidified. The yield was 56 g. This was recrystallized from ethanol-ethyl acetate (3:1 volume) to obtained (I). mp 92°C.

The analytical values were C: 91.85%, H: 8.18%.

The calculated values in terms of $C_{24}H_{20}$ were C: 91.67%, H: 8.33%.

Synthesis of bis(phthalic acid) Derivative (II) /1070

Quantities of 10.6 g of (I) and 132 g of 30% HNO_3 were put into an electromagnet stirring type autoclave with a volume of 200 ml, and the temperature was raised to 200°C in about 1 hour. When the pressure increased above 25 kg/cm^2, degassing was performed, and the temperature was kept at 200°C for 4 hours. After cooling, the contents were removed, and the precipitate was filtered and rinsed. The precipitate was then dissolved in 400 ml of a 10% aqueous solution of sodium hydroxide. Concentrated hydrochloric acid was added to this filtrate to render it acidic. At this time, the acid was separated. The separated precipitate was filtered and further dissolved in a 10% solution of sodium hydroxide. When hydrochloric acid was added to this filtrate, the precipitate which separated when it had been made slightly acidic was centrifuged and collected. Rinsing was repeated until all chlorine ions had completely disappeared from the washings. The separated precipitate was dried at 90°C and 1 mm Hg. The mp was 300°C or higher. In the IR spectra, there were characteristic absorption bands at 2900-2500 cm^{-1} (carboxyl group association OH) and 1700 cm^{-1} (carboxylic acid $\nu_{C=O}$), as is indicated in Fig. 1.

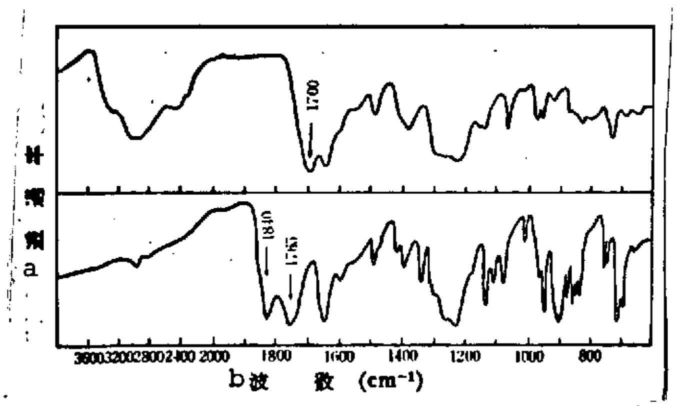

Fig. 1. IR spectra of II and III (KBr capsules).

Key: a. Transmittance; 2. Wavelength (cm^{-1})

The analytical values were: C: 62.50%, H: 3.52%.

The calculated values in terms of $C_{24}H_{14}O_{10}$ were: C: 62.34%, H: 3.05%.

<u>Synthesis of bis(phthalic anhydride) Derivative (III)</u>

Tetracarboxylic acid (II) was treated for 8 hours at 0.5 mm Hg and 200-230°C, resulting in acid dianhydride (III). In the IR spectra, as shown in Fig. 1, carbonyl characteristic absorption by the acid anhydride was observed as a doublet at 1840 cm^{-1} and 1765 cm^{-1}. There was no 1700 cm^{-1} absorption band by tetracarboxylic acid.

The analytical values were: C: 67.40%, H: 2.58%.

The calculated values in terms of $C_{24}H_{10}O_8$ were: C: 67.61%, H: 2.36%.

2.2. The Condensation Reaction

The reaction between equimolar diamine and the acid anhydride (III) took place in a polar solvent of N-methyl pyrrolidone (abbreviated as NMP). The NMP was thoroughly dried in advance on phosphorus pentoxide and was then rectified at reduced pressure in nitrogen. Diamine (0.004 mol) was dissolved in 60 ml of NMP in a flask with four mouths with a volume of 150 ml, and 1.704 g (0.004 mol) of (III) was added, small quantities at a time, at room temperature in a nitrogen current. After addition of (III), the temperature was raised to 50°C, and it was stirred for 3 hours. The contents became a uniform, dark-brown solution, and the viscosity rose. When acetone or alcohol was added to this NMP solution as a nonsolvent, the polymer was precipitated. The precipitate was filtered, washed with acetone, given heat treatment at 130°C for 3 hours and then for 8 hours at 200°C and 0.5 mm Hg, and made into a polyimide.

The NMP solution mentioned above was heated without modification for 3 hours at 150°C, but no polyimide precipitate was separated as occurred in the case of polypyromellitaminic acid [1].

2.3. X-Ray Diffraction

Films with a thickness of about 0.03 mm were measured with a recording X-ray analyzer (Shimadzu GX-2). The films were put into window frames measuring 20 × 15 mm under the following conditions: acceleration voltage 35 kV, current 10 mA, slit width 0.2 mm, FeK_{α} rays, filter Mn, time constant 5 sec.

2.4. Measurement of Electrical Properties

The NMP-soluble polymer solution (described in Section 2.2) was poured onto aluminum plates and heated for 2 hours at 135°C and for 2 hours at 200°C. The process of pouring and heating was repeated until uniform films with a thickness of 0.25 ± 0.01 mm were obtained. The electrodes were formed by vacuum deposition of metallic aluminum in a circle with a diameter of 20 mm on the upper surfaces of these films. To form the guard electrodes, evaporation deposition was performed in the form of concentric circles (inner diameter 50 mm, outer diameter 60 mm).

The resistance was measured by applying DC voltage of 100 V, and the current (1-min value) was measured with a micro-micro [sic] ammeter (model TR-15, Takeda Riken). The surface leakage current was removed by the guards.

Both the dielectric constant and the dielectric loss tangent were measured by means of a broad-band electrical loss measuring instrument (Ando Denki), using the same samples.

2.5. Thermobalance

The final heat-treated products prepared in Section 2.2 were made into a powder of about 100 mesh. Pyrolysis was performed with a model TB-10 instrument (Shimadzu) at a heating rate of 3°C/min from room temperature to 600°C. In cases when the atmosphere was nitrogen, the system was evacuated in advance and nitrogen was substituted. The flow rate was 12-15 ml/min.

3. Results and Discussion

3.1. Formation of Polyphthalimides

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3.1. Formation of Polyphthalimides

The NMP-soluble polymers IVa' and IVb', which were formed in the reaction between the acid dianhydride (III) and diaminodiphenyl ethyl or diaminodiphenyl methane in NMP, had a reduction viscosity η_{sp}/c (NMP 0.5% solution, 25°C) of 0.92 and 0.85, respectively.

When NMP solutions of these polymers IVa' and IVb' are coated on metal plates, they can be transformed into films easily by processing at reduced pressure at room temperature. When they are processed for longer than 4 hours at 200°C, polyimides will be produced, as will be mentioned below. In both of these cases, tough, yellow films with abundant flexibility were produced. When they were heated to 300°C, no melting or other changes in appearance were observed, and they were insoluble in formic acid, dimethyl acetamide, dimethyl sulfoxide, and NMP.

In Fig. 2 are shown the IR spectra when the NMP soluble polymer IVa' was coated on an infrared cell plate and heating was performed in the following three stages

(1) heating for 3 hours at 50-60°C at reduced pressure (0.5 mm Hg)

(2) (1) + 130°C for 30 min

(3) (2) + 220°C for 4 hours. /1071

In Fig. 2, the 1500 cm^{-1} absorption band (aromatic nucleus $\nu_{C=C}$) marked with ⊙ retains almost the identical intensity even when heated. However, among those with decreased absorption intensity or which lose their absorption intensity (these are marked with ↑), 3260 cm^{-1} corresponds to the N-H absorption band,

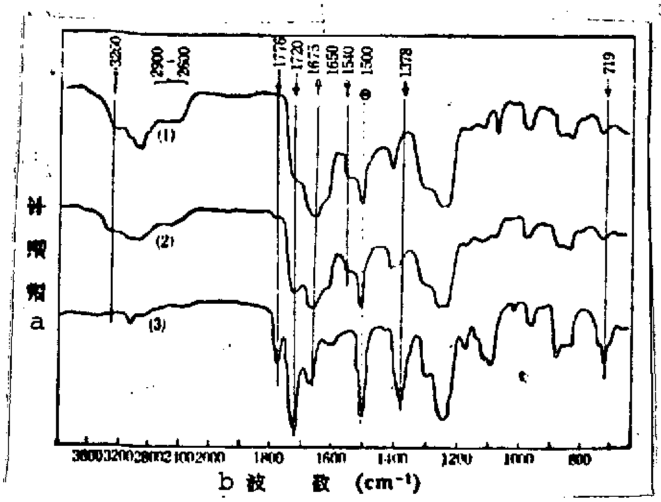


Fig. 2. Changes in IR spectra with heating of IVa' (film)
(1) 0.5 mm Hg, 50°C, 3 hours;
(2) (1) + 130°C, 30 min;
(3) (2) + 220°C, 4 hours

Key: a. Transmittance;
2. Wavelength (cm^{-1})

2940-2600 cm^{-1} corresponds to the OH(-COOH) absorption band, 1675-1650 cm^{-1} corresponds to the amide I absorption band, and 1540 cm^{-1} corresponds to the amide II absorption band. Those in which the intensity increases or appears are marked with ↓. They include 1776 cm^{-1} (imide I $\nu_{C=O}$), 1720 cm^{-1} (imide II $\nu_{C=O}$), 1378 cm^{-1} amd 719 cm^{-1}. All of them correspond to the absorption bands which appear during the formation of poly-pyromellitic imides, as was reported previously [3]. It is believed that they indicate the formation of the phthalimide ring. The fact that the 1672 cm^{-1} absorption band remains indicates a characteristic absorption band of benzophenone type carbonyls. In IVa, the absorption band due to the -O- radical appears strongly at 1245 cm^{-1}, and in IVb $-CH_2-$ appears very weakly at 2900 and 2800 cm^{-1}. These each correspond to these respective structures.

As was mentioned above in Section 2.2, the anlytical values of N in the specimens heated at reduced pressure correspond quite well to the calculated values for polyphthalimide by equation (1).

It is clear from these results that, just as in cases when polypyromellitic imides are formed [3], there is passage through phthalamidic acid, as in equation (1), and there is conversion to the phthalimide ring by means of ring closure condensation.

3.2. Hydrolysis of Polyphthalimides

Findings concerning the decomposition of the IVa films, which had been completely converted into imides (film thickness about 0.015 mm), in alkaline aqueous solutions were obtained from the IR spectra when processing was carried out in the following stages (Fig. 3).

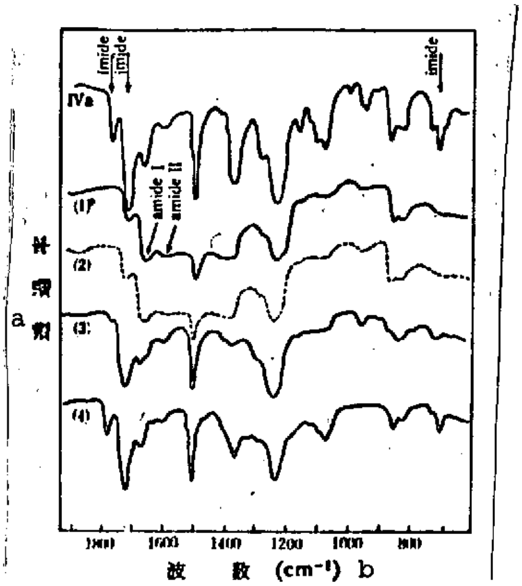


Fig. 3. Changes in IR spectra with hydrolysis of IVa (film): (1) Immersed for 12 hours in 10% NaOH solution at room temperature, dried; (2) (1) + 220°C, 4 hours; (3) (1) + immersed for 20 min in 1N HCl, dried; (4) (3) + 220°C, 4 hours.

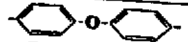
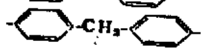
(1) After they had been immersed at room temperature in a 10% aqueous solution of sodium hydroxide for 12 hours, they were rinsed lightly and dried at reduced pressure (1 mm Hg).

(2) After (1), they were heated for 4 hours at 220°C.

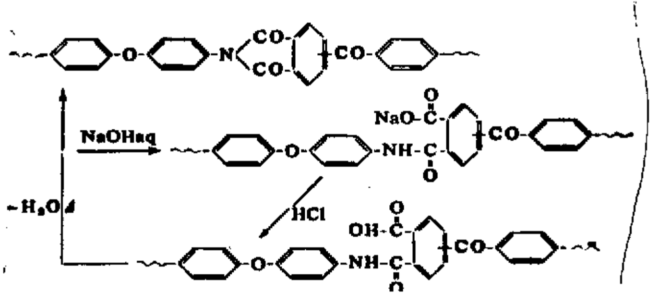
(3) After (1) [sic], they were immersed for 20 min in 1N hydrochloric acid at room temperature. Then they were rinsed lightly and dried at reduced temperature (0.1 mm Hg).

(4) After (3), they were heated for 4 hours at 220°C.

TABLE 1. ANALYTICAL VALUES OF POLYPHTHALIMIDES

Diamine components R	N% Calculated values	N% Analytical values
	4.74	4.96, 4.91
	4.76	4.71, 4.92

When processed in stage (1), poly-[N,N'(p,p''-oxydiphenylin)--pyromellitic imide] will change into a grease [6]. However, the polyphthalimides here, both IVa and IVb, will retain their film shape, will lose their yellow color, and will become colorless and transparent. The 1776, 1720, 1378, and 719 cm^{-1} bands due to the imide base will all be reduced or will disappear completely, while bands will appear at 1675-1650 cm^{-1} (amide I absorption band). Even in processing in stage (3), they will retain a colorless film state, and the IR spectrum here will be exactly the same as (1) in Fig. 2. This indicates that this is an amidic acid type of IVa'. When this is given heat treatment in stage (4), it will again become the original yellow, flexible film. The IR spectrum indicates that this is polyphthalimide IVa. However, the IR spectrum remains almost unchanged in processing in stage (2). This indicates that it is difficult to cyclize and imidize it, even by heat treatment for 4 hours at 220°C. That is, it is believed that the polyimide is alkaline and can undergo hydrolysis relatively easily, that ring opening occurs as shown in the following formula, that it is converted into polyamidic acid when given acid treatment, and that this will again undergo ring closure condensation when heated.



3.3. X-Ray Diffraction

X-ray diffraction was performed in order to study the film crystallinity of IVa and IVb. The results showed that both of them were amorphous.

3.4. Electrical Properties

The electrical properties of the polyphthalimide IVa and IVb films are shown in Table 2. The values are those at room temperature (23-25°C) and at a relative humidity of 65%.

TABLE 2. ELECTRICAL PROPERTIES OF POLYPHTHALIMIDES

	Polyphthalimides	
	IVa	IVb
Specific volume resistivity -cm	$10^{16}\sim10^{17}$	$10^{16}\sim10^{17}$
Dielectric constant (50 c)	6.13	7.77
Dielectric loss tangent tan (50 c)	0.0045	0.0113
Dielectric breakdown voltage kV/0.1 mm	14~18	14~17

The temperature dependence of the electrical resistance of IVa, as shown in Fig. 4, within the range of 100-230°C, followed a linear relationship of $\rho = \rho_0$ exp E/kT, and its activation energy E was 0.92 eV. The frequency dependence of the dielectric constant and the dielectric loss tangent is shown in Fig. 5. Among these electrical properties, it is noteworthy that these polyphthalimides have high values of 6.1-7.8 for the dielectric constant, as compared with values of 3.1-3.7 (1 kc, 23°C) for poly-[N,N'(p,p'-oxydiphenylin) pyromellitic imide] [4].

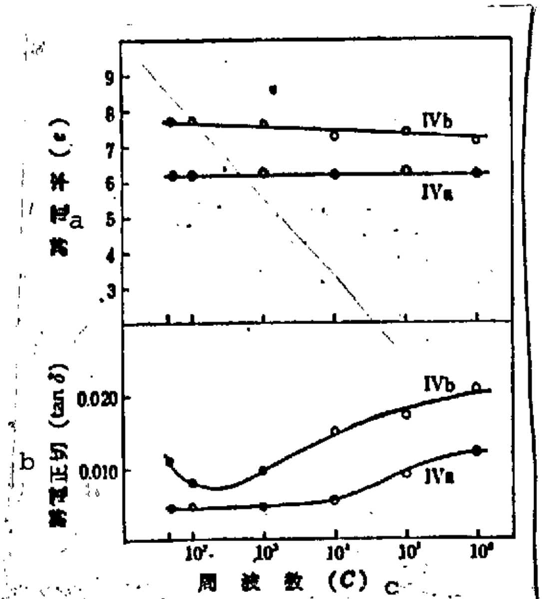


Fig. 4. Frequency dependence of dielectric constant and dielectric loss tangent of polyphthalimide IVa and IVb.

Key: a. Dielectric constant; b. Dielectric loss tangent; c. Frequency

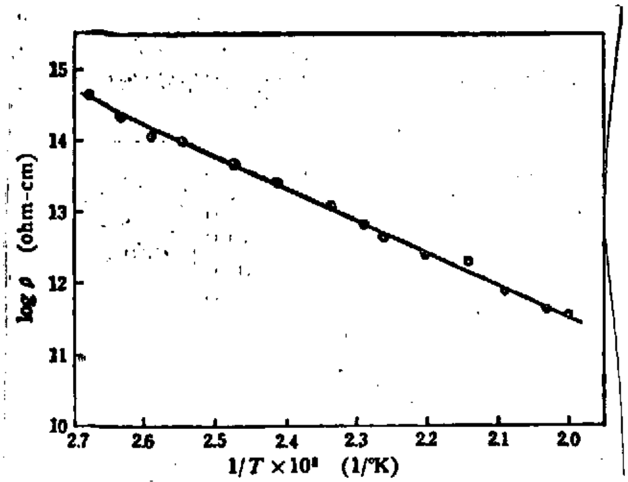


Fig. 5. Temperature dependence of electric resistance of polyphthalimide IVa.

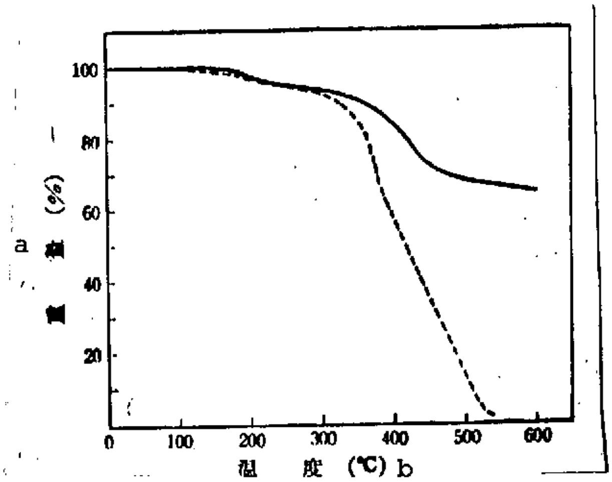


Fig. 6. Thermobalance curves of IVa
ΔT: 3°C/min,
——: in nitrogen,
----: in air

Key: a. Weight (%)
b. Temperature (°C)

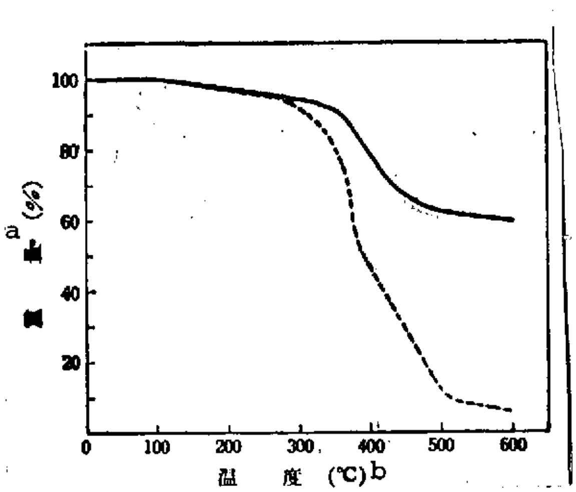


Fig. 7. Thermobalance curves of IVb
ΔT: 3°C/min, ——: in nitrogen,
----: in air.

Key: a. Weight (%); 2. Temperature (°C)

3.4. [sic] Pyrolysis

In order to study the thermal stability of the polyimides formed, the weight loss during heating was measured at a constant temperature increase (3°C/min). The results for IVa and IVb in the air and in nitrogen are shown in Figs. 6 and 7. For both IVa and IVb, there was the greatest weight reduction speed in the vicinity of 370-380°C in the air and in the vicinity of 390-420°C in nitrogen. Especially in the air there is almost complete decomposition and volatilization up to 10% at /1072 temperatures of up to 500°C. It is believed that decomposition based on these breaks in the main chain commences at temperatures above 350°C.

Measurements of the dielectric constant were carried out with the collaboration of Mr. Keizo Sakata of this institute.

REFERENCES

1. Nishizaki and Fukami, Kōgyō kagaku zasshi 66, 382 (1963).

2. Nishizaki and Fukami, Kōgyō kagaku zasshi 67, 474 (1964).

3. Scala, L. C. and Hickam, W. M., J. Appl. Polymer Sci. 9, 245 (1965).

4. Sroog, C. E., Endrey, A. L., Abramo, S. V., Berr, C. E., Edwards, W. M., and Olivier, K. L., J. Polymer Sci. Pt. A 3, 1373 (1965).

5. Nishizaki, S. and Fukami, A., Mitsubishi Denki Laboratory Reports 4, 521 (1963).

6. Nishizaki, unpublished manuscript.